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STRUCTURAL AND MECHANICAL EFFECTS OF RADIATION EXPOSURE ON FILLED ELASTOMERS - RECENT INSIGHTS FROM EXPERIMENTS AND MODELING

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STRUCTURAL AND MECHANICAL EFFECTS OF RADIATION EXPOSURE ON FILLED ELASTOMERS – RECENT INSIGHTS FROM EXPERIMENTS AND MODELING

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Introduction

Filled and cross-linked elastomeric rubber and foam are versatile network materials with multitude of applications ranging from artificial organs and biomedical devices to cushions, coatings, adhesives, interconnects, and seismic-isolation-, thermal-, and electrical barriers. However, upon long-term or repeated exposure to external factors like mechanical stress, temperature fluctuations, or radiation such materials can undergo chemical aging. The most profound aging signatures include: (1) creation of new cross-links; (2) breaking (scission) of covalent bonds; and (3) modification of the polymer-filler interface. All these can directly affect the molecular weight distribution (MWD) of the polymer between cross-links or physical restraints, thereby altering and degrading many of the useful properties it was originally designed for. In spite of great advances in the statistical theories of the polymer network, there has been relatively little experimental literature on the microscopic structural details of such materials. For instance, the MWD between cross-link junctions and other physical restraints (like entanglements) is virtually unknown for most network materials. Thus, it is a scientific and technological challenge to understand how cross-linking and chain scissioning induced by external effects mentioned above can affect the MWD of polymer networks. In this work, we use an array of experimental techniques to measure the stress-strain response, permanent set, and MWD for rubber samples subjected to controlled radiation dosages. We show that the observed radiation-induced changes in the mechanical and elastic properties can be described with quantitative accuracy using a simple network model. We show how such a model allows an elegant interpretation of the experiments, and yields the rate of radiation-induced bond scissioning processes at the molecular scale. Finally, we incorporate such rates into a mesoscopic network model in an attempt to simulate the radiation-induced evolution of the MWD.

Permanent set and stress-strain measurements

Thin rectangular samples of a commercial PDMS-based rubber (TR-55 from Dow Corning) were stretched to specific strain levels and exposed to controlled dosages of γ-radiation from a Co-60 source (1.4MeV, 0.5Mrad/hour dose rate) in a non-reactive nitrogen atmosphere. Seven different strain levels were studied, corresponding to stretch ratios λ_1 = 1.20, 1.47, 1.67, 1.84, 2.00, 2.33, 2.67. Following exposure to controlled duration (and therefore dosages) of radiation, each sample was removed from the irradiation chamber, released from the λ_1-strain, and allowed to relax at ambient conditions for a week. The relaxed samples were then subjected to two different sets of measurements [1]: (1) the new equilibrium length, called the recovered length λ_s, followed by (2) stress-strain analysis for strains of up to 50% elongation (using a TA Instruments ARES LS-2 rheometer in torsion rectangle geometry). Fig. 1 plots the measured recovered length (λ_s) as a function of radiation dosage D for the different values of λ_1. Error bars indicate sample-to-sample variation in cases where multi-sample measurements were performed.

Fig. 2 plots a typical stress-strain response of such samples (only the loading curves are shown and the unloading curves hidden for clarity). The main feature is that there is strong dependence on the cycle number. In particular, in cycle 1 the response is much steeper, corresponding to a significantly higher elastic modulus, while the response becomes progressively softer in subsequent cycles, but with a much smaller drop-off than between cycle 1 and cycle 2. This type of softening has long been known to occur in filled rubber materials and is generally known as the Mullins effect. At the end of cycle 1 a small permanent stretch (~ 2%) is also incurred, which is smaller than typical permanent sets reported in Fig. 1. It is important to note here that the recovered length in Fig. 1 was obtained *prior* to subjecting the samples to the stress-strain cycles as in Fig. 2.

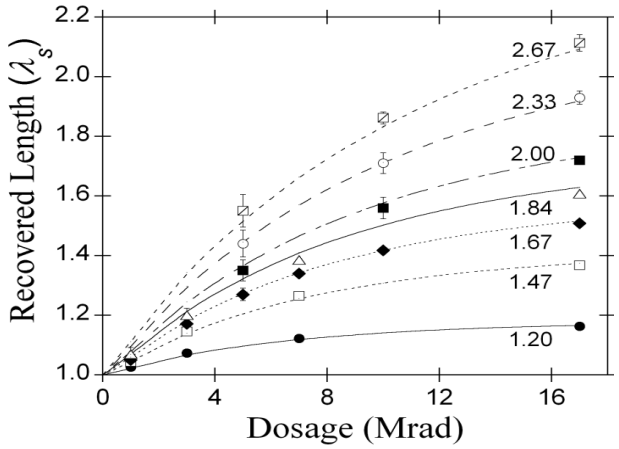

Figure 1. Permanent set data (in terms of recovered length) for different strain levels at which the elastomer is subjected to radiation. The lines are theoretical results using a Neohookean materials model.

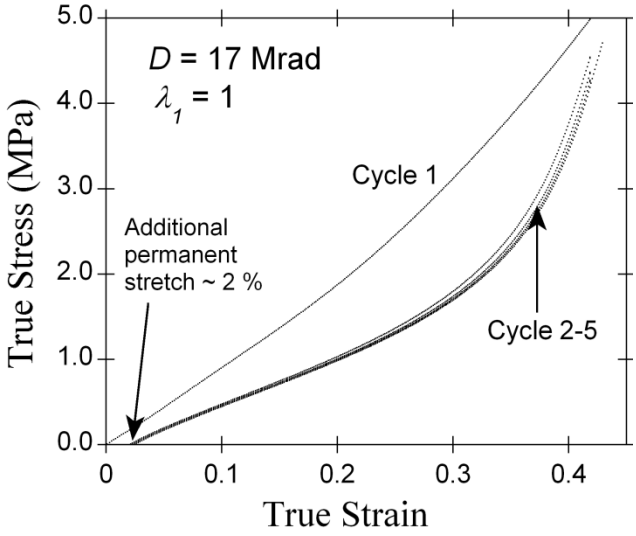

Figure 2. Typical stress-strain response of a radiation-exposed TR-55 sample through the first five cycles. The data shown corresponds to a sample that was exposed to 17 Mrad of radiation (under λ_1 = 1) and then stretched to a maximum of 50% of its original length during each cycle.

Next the Young's modulus (E) was extracted from the stress-strain *slope* at small deformation (corresponding to strain levels of 5% or less) for various cycles and various values of λ_1 and D. Fig. 3 displays the results for E in cycles 1 and 5. We observe the following trends: (1) for all values of λ_1 the modulus increases as a function of D within each cycle. For λ_1 = 1 and cycle 1 this increase is nearly linear; (2) for all values of λ_1 and D the modulus significantly decreases from cycle 1 to cycle 5, similar to the softening behavior seen in Fig. 2. This decrease in modulus is the largest for λ_1 = 1 and gets progressively smaller for increasing values of λ_1; (3) as a function of λ_1 the modulus displays a complex behavior that can be increasing, decreasing, or non-monotonic depending upon the cycle and the radiation dosage D. In particular, in cycle 1 the modulus E shows an overall decreasing trend as a function of increasing λ_1, with the rate of decrease $|\partial E/\partial \lambda_1|$ getting smaller with increasing λ_1 and increasing D. In cycle 5 on the other hand E shows more complex behavior as a function of λ_1, decreasing at D = 5 Mrad, increasing at D = 17 Mrad, and non-monotonic at intermediate values (10 Mrad). The above behavior of E can be traced to a combination of two effects: (i) material softening due to the Mullins effect; and (ii) radiation

hardening of the elastomer due to the creation of a net number of new cross-links.

MQ-NMR measurements

In order to experimentally determine the MWD between junctions/ restraints, we utilized the technique of ^{1}H multi-quantum NMR (MQ-NMR), which allows for the quantification of dipolar couplings between protons not averaged to zero due to rapid, but anisotropic motion of the polymer chains. The anisotropic dynamics are due to chemical and physical restrains (due to cross-links and entanglements, respectively). Recent work [2] has established that MQ-NMR based quantification of the residual dipolar couplings in silicone elastomers is very robust, with the following relationship between the residual dipolar coupling (Ω_d) and the number of statistical segments between crosslinks (p):

$$\frac{\langle \Omega \rangle}{\langle \Omega_0 \rangle} = \langle P_2(\cos\alpha) \rangle \approx \frac{3r^2}{5p}, \qquad (1)$$

where $\langle\ \rangle$ denotes averaging over all chain orientations, Ω_0 is the dipolar coupling in the absence of motion (pre-averaged by the fast motion of the methyl group), P_2 is the second-order Legendre polynomial, α is the angle between the dipolar vector and the chain axis (i.e., the angle between the backbone chain axis and the Si-C vector), and r is the length of the end-to-end vector, |R|, expressed as a ratio to that of the unperturbed melt, $|R_0|$, *i.e.*, $r = |R|/|R_0|$. Taking the number of monomers in a statistical segment to be 5.7, the MWD can be determined from MQ-NMR measurements using eq. (1). Fig. 5 displays the MQ-NMR spectra for the virgin material as well as for samples exposed to various radiation dosages. The intensity (y-axis) is proportional to the number of monomers in each chain-segment. Thus the area under each curve is proportional to N, the total number of monomers in the system. It is convenient to define a normalized MWD $n(p, D)$ (where p = # monomers between crosslinks and D = radiation dosage), such that a normalized NMR intensity is equal to $pn(p, D)$, and the total area under each curve is 1. All curves in Fig. 5 (i.e. for each D) are normalized in this way.

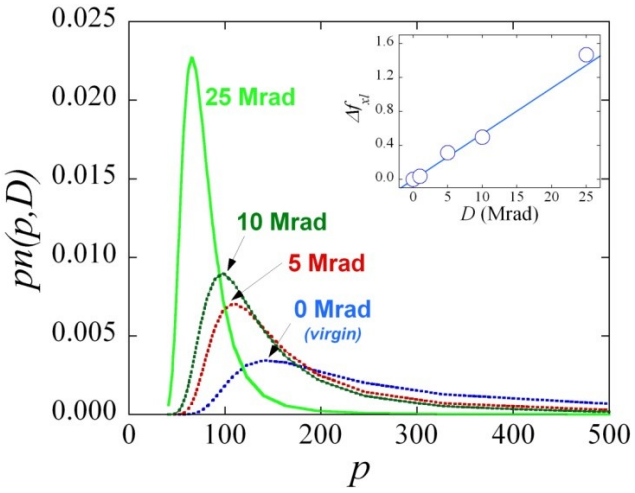

Figure 3. MWD ($pn(p,D)$) from MQ-NMR measurements for various radiation dosages. Inset: Corresponding chain density increment: $\Delta f_{xl} = p_{av}(0)/p_{av}(D) - 1$ as a function of D; solid curve: $y = C_0D$, see ref. [3].

Constitutive and Mesoscale modeling

To analyze the above experimental data we adopted the Neohookean stress response model defined by the function $\sigma = G(\lambda - 1/\lambda)$ where σ is the (true) stress under a uniaxial stretch ratio λ, and G is the shear modulus that depends on the cross-link density in the material. The creation of cross-links at a strained state λ_1 was taken into account by employing a 2-stage independent network model modeled after Tobolsky, from which an explicit expression for the recovered length (λ_s) can be derived. Starting from a pristine MWD we show that the experimental results on radiation hardening can be elegantly explained by a constant radiation-induced molecular-scale cross-linking probability per monomer per unit radiation dosage [3]. Finally, we describe how such molecular rates can be incorporated into a recently developed mesoscale network model [4] to directly simulate the evolution of elastomeric network under the exposure to radiation.

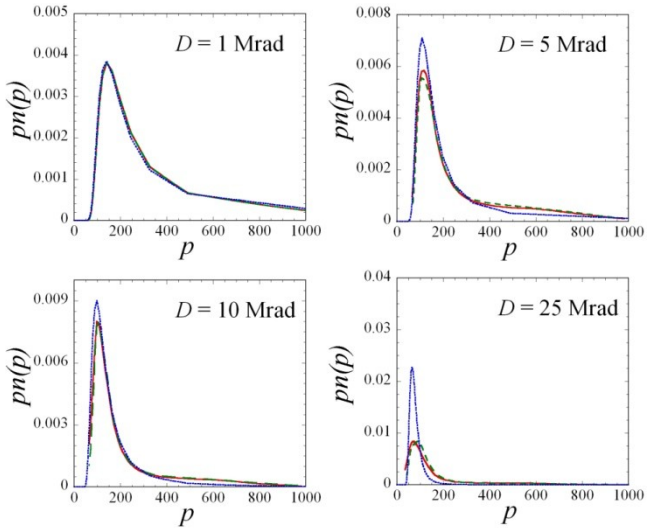

Figure 4. Comparison of experimental MWD of Fig. 3 (blue line) with computed MWD for fourfold-linking only (red solid line) and threefold-linking only (green dashed line).

Conclusions

Our work demonstrates that the exposure of elastomeric rubber materials to controlled dosages of radiation can alter mechanical properties in a reproducible and predictable manner. The newly developed technique of multi-quantum NMR enables accurate characterization of MWD between cross-links (or physical restraints), which along with a simple, yet elegant network model and mesoscale simulations provide useful insights into radiation-induced modifications at the molecular level. For our specific rubber material the NMR data up to 10 Mrad appears consistent with either fourfold- or threefold-connected junctions, with the presence of dangling bonds, loops, or small volatile species becoming possibly important at much higher dosages. Interesting trends in the measured Young's modulus is observed as a function of radiation dosage and the strain at which the radiation exposure is performed. More specifically, at lower radiation dosages and earlier stress-strain cycles the modulus is found to decrease with increasing strain of exposure, while the trend gets reversed at higher dosages and later cycles. We show that the above behavior arises due to the interplay of two opposing effects, i.e., materials *softening* due to the Mullins effect and radiation *hardening* due to the creation of new cross-links. Experimental control and insights such as these are hoped to create novel opportunities and applications in the field of radiation-controlled manipulation of material properties.

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